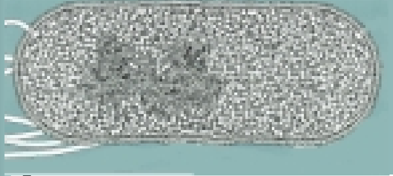


Today's Lecture

1) Review of entropy
2) The Third Law
3) Brief review of the Second Law
4) Gibbs Free Energy

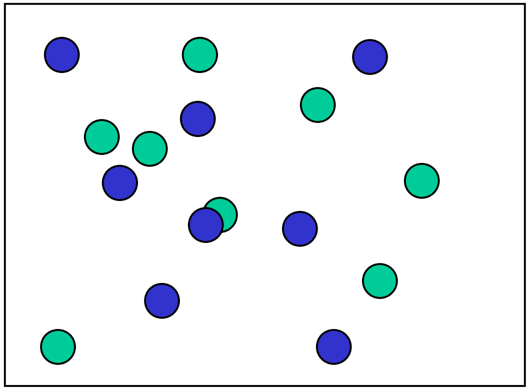
Entropy

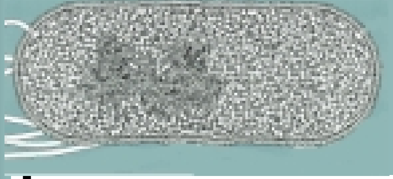
Recall from last week:

- Entropy (symbol S) is a state function
- Defined by

$$dS = \frac{dq_{\text{rev}}}{T}$$

- A measure of disorder on the molecular level



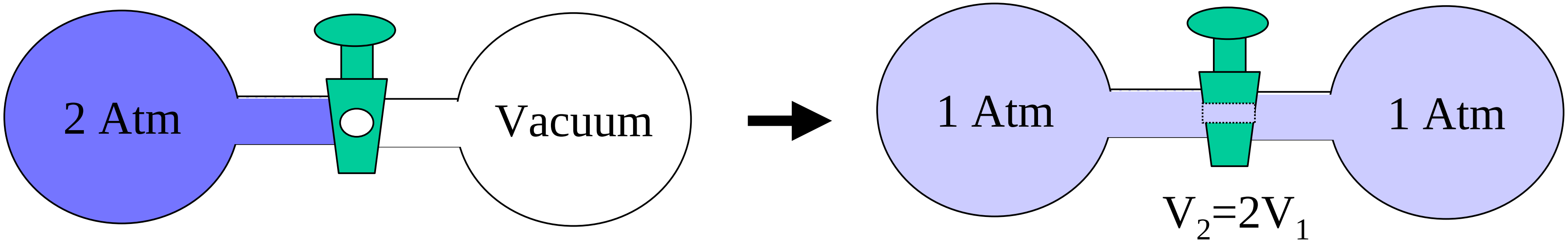


Entropy calculations

To find the entropy change ΔS between two states:

1. Find a reversible path between them.
2. Compute q/T for this path

Last week's example: Expansion into a vacuum

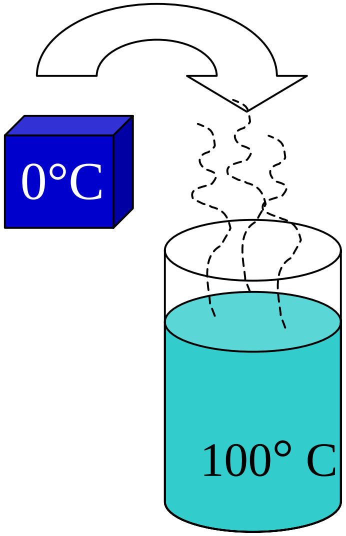


Irreversible path: $q,w = 0$ so $\Delta S = 0$ (wrong!)

Reversible path: $w = -RT\ln 2$, $q = -w$ so $\Delta S = R\ln 2$ (right!)

Entropy calculations

Another example: dropping an ice cube into boiling hot water.

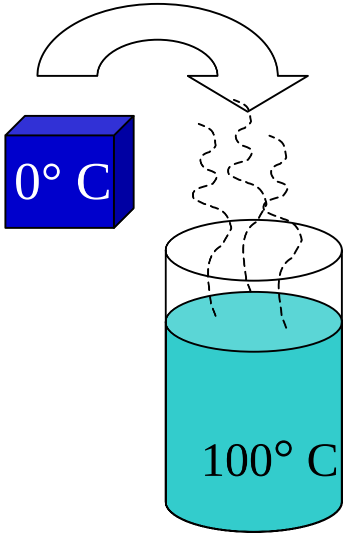


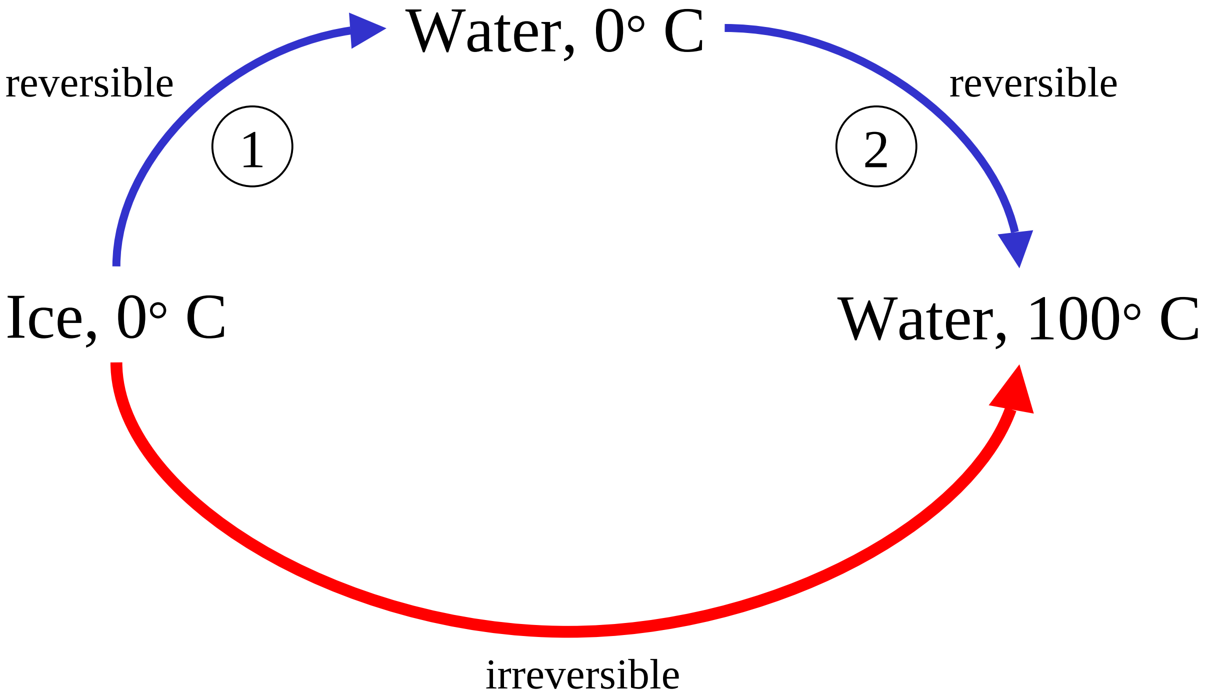
What happens?

Is it reversible?

Let’s take the ice cube as the system, and the hot water as the surroundings (i.e. there’s enough hot water so that it stays 100° C).

Entropy calculations





Water, 0° C

reversible

①

reversible

②

Ice, 0° C

Water, 100° C

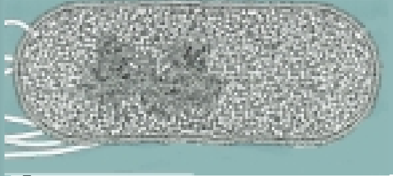
irreversible

Let’s calculate for the reversible path...

Entropy calculations

① Entropy of phase transition

$$
\begin{aligned}
q &= \Delta H \\
\Delta S &= \Delta H / T \\
&= \left(6\ \mathrm{kJ\ mol^{-1}}\right) / \left(273\ \mathrm{K}\ \right) \qquad \text{(for water)} \\
&= +22\ \mathrm{J\ mol^{-1}\ K}
\end{aligned}
$$



Entropy calculations

② Entropy of heating

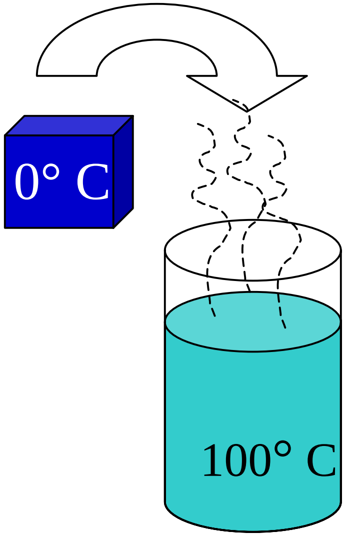
$$dq = C_P dT$$

$$\Delta S = \int_{T_1}^{T_2} C_P \frac{dT}{T}$$

$$= \left(75.3\,\mathrm{J\ mol^{-1}\ K}\right)\ln\left(\frac{373}{273}\right)$$

$$= +23.5\,\mathrm{J\ mol^{-1}\ K}$$

Entropy calculations

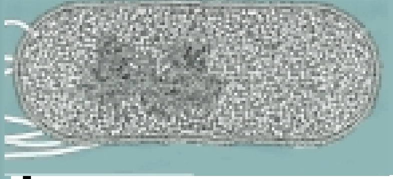


Altogether, $\Delta S = ① + ②$

$= 45.5 \text{ J K}^{-1} \text{ mol}^{-1}$

Remember, this is only for the *system* (ice cube).

Is this process spontaneous?
It better be… How can we tell?



Entropy calculations

Entropy change in the surroundings:

How much total heat was exchanged with the surroundings?

For melting, $-6\ \text{kJ mol}^{-1}$.

For heating, $-0.75\ \text{kJ mol}^{-1}$. *This is just* $C_P(T_2 - T_1)$

Total = $-6.75\ \text{kJ mol}^{-1}$.

$$\Delta S = -6750\ \text{J mol}^{-1} / 373\ \text{K}$$

$$= -18.1\ \text{J mol}^{-1}\ \text{K}^{-1}$$

Total entropy change for the universe: $+27.4\ \text{J mol}^{-1}\ \text{K}^{-1}$

whew… We’ll get back to the Second Law later.

The Third Law of Thermodynamics

There is an absolute reference point for entropy!

Walther Nernst
(1864-1941)
Nobelist, 1920

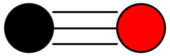
The Third Law states:
“The entropy of a perfect crystal at 0 K is zero.”

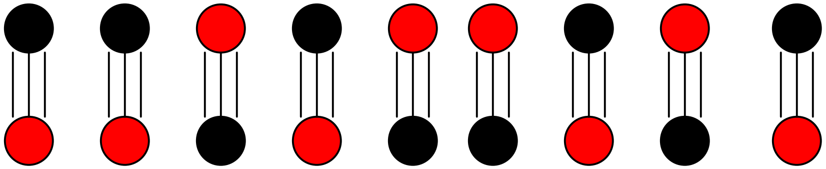
More precisely, it states that the entropy of all perfect crystals at absolute 0 is *the same*, so we might as well call it zero. Molecular (stat mech) considerations show that zero is a good thing to call it.

The Third Law

A couple of Third-Law points:

- ***Just cooling something to 0 K is not enough.***

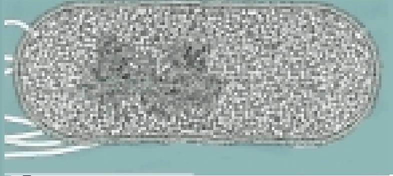
Example: Carbon monoxide 



Not a perfect crystal !!!

- ***Elements, compounds, it's all zero!***

Unlike E, the reference state for S is a perfect crystal of a *pure substance*, not necessarily an element.



The Third Law

The Third Law makes sense from the molecular point of view:

- A perfect crystal has only one possible arrangement of atoms.
- At 0 K there is only one possible distribution of energy.

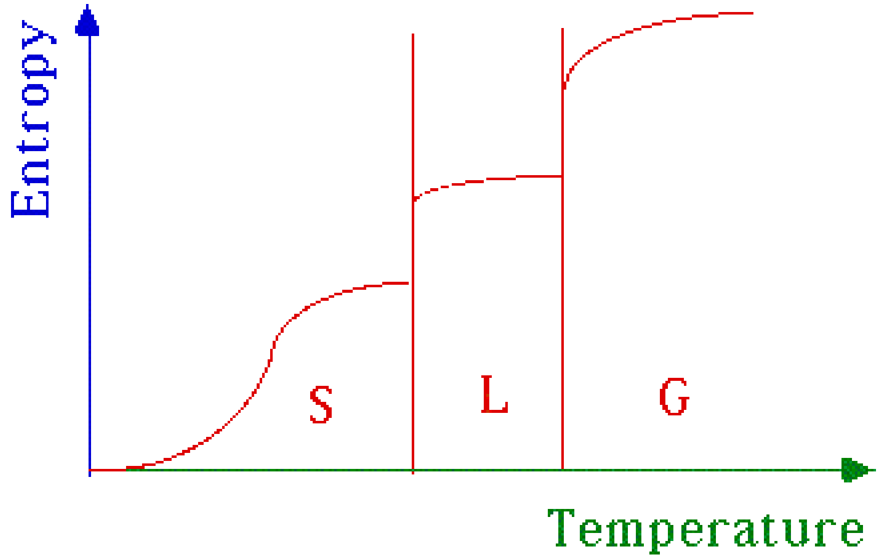
$$\Omega = 1$$

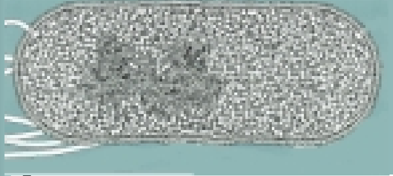
$$\ln\Omega = 0$$

The Third Law

What good is the Third Law?

It lets us calculate the entropy of any substance in any state!





Back to the Second Law

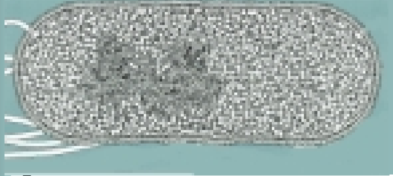
The Second Law:

$$\Delta S \geq 0$$

The entropy of a ***closed system*** can only increase.

If a process will decrease entropy in a closed system, then it does not occur spontaneously. Its *opposite* will occur spontaneously.

But we very rarely work with closed systems...



Back to the Second Law

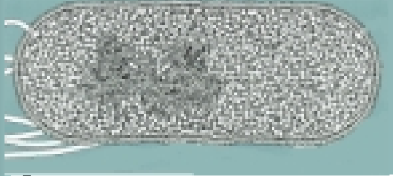
…except for the universe as a whole!

$$\Delta S_{sys} + \Delta S_{surr} \geq 0$$

The entropy of a system can spontaneously decrease, as long as the entropy of the surroundings increases by at least as much.

Do we have to keep calculating ΔS_{surr} ?

Not necessarily!



Constant temperature and pressure

Let’s stay at constant T and P:

$$\Delta S_{\mathrm{surr}} = -\frac{q_P}{T} = -\frac{\Delta H}{T}$$

$$\boxed{\Delta S_{\mathrm{tot}} = \Delta S_{\mathrm{sys}} - \frac{\Delta H}{T}}$$

Now everything is in terms of the *system*. The criterion for spontaneity given by the Second Law becomes:

$$\Delta S_{\mathrm{tot}} \geq 0 \Leftrightarrow \Delta S_{\mathrm{sys}} - \frac{\Delta H}{T} \geq 0$$

Gibbs Free Energy

The Gibbs Free Energy is a new state function, defined as:

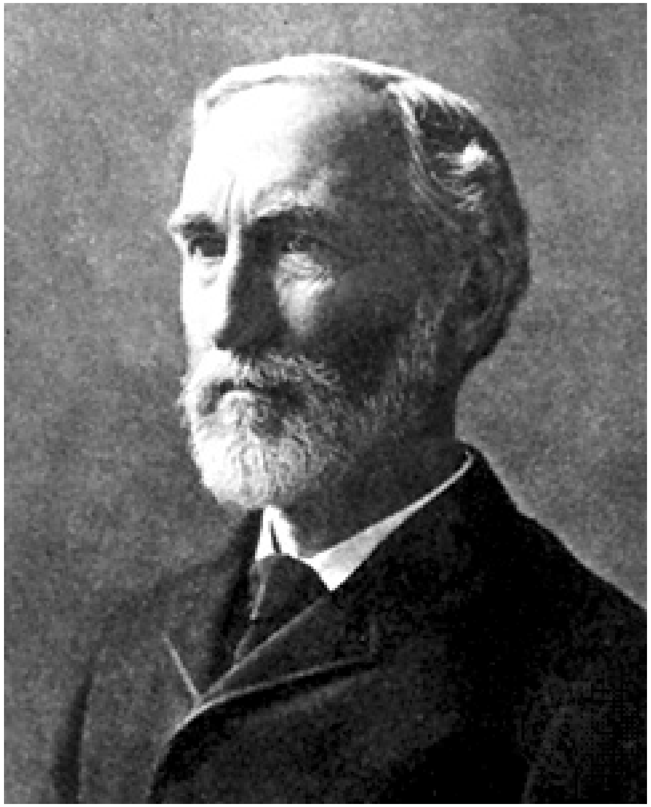
$$G \equiv H - TS$$

At constant temperature and pressure, ΔG is

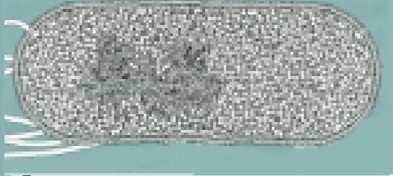
$$\Delta G = \Delta H - T\Delta S$$

From the previous slide, we end up with

$$\boxed{\Delta S_{\mathrm{tot}} \geq 0 \Leftrightarrow \Delta G \leq 0}$$



Josiah Willard Gibbs
(1839-1903)



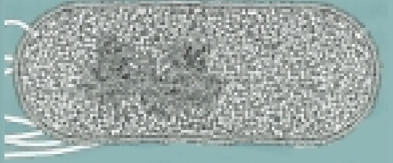
Gibbs Free Energy

G is extremely useful for chemistry and biochemistry, since so much takes place at constant temperature and pressure.

The condition of **constant T and P** is **very important** when using G. Otherwise, the entropy change of the surroundings might be different and we might get the **wrong answer**

(However, G is still defined and can be calculated for any change of state, including changing P and T. More later…)

At constant T and P, consideration of ΔG will answer the question "Will a given reaction be spontaneous?"



Calculation of ΔG

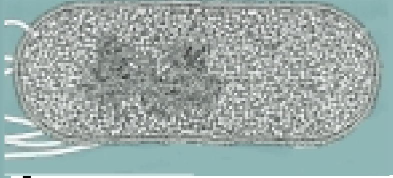
In many cases, we can build on calculations we have already done in order to get ΔG.

$$\Delta G = \Delta H - T\Delta S$$

Example: ice melting at 100° C

$\Delta H = 6.75\ \text{kJ mol}^{-1}$
$\Delta S = 45.5\ \text{J K}^{-1}\ \text{mol}^{-1}$
so
$\Delta G = 6750 - (373)(45.5)$
$= -10.2\ \text{kJ mol}^{-1}.$

In other cases, like chemical reactions, standard values have been found. We need only to add them up properly.

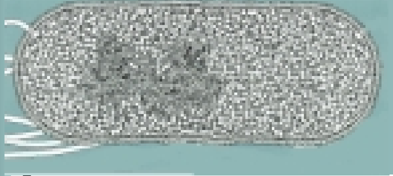


Calculation of ΔG

Example: $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

ΔG°_f -50.7 0 -394.36 -228.6

$$\Delta G^\circ_r = -800 \text{ kJ mol}^{-1}$$



Calculation of ΔG

Sometimes we have to work with G directly. To the calculus!

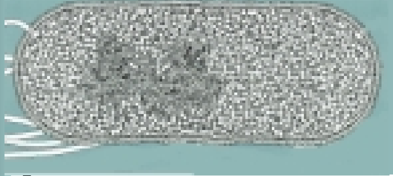
$$\begin{aligned} dG &= dH - TdS - SdT \\ &= dE + pdV + Vdp - TdS - SdT \end{aligned}$$

but $dE = -pdV + TdS$

so $dG = Vdp - SdT$

In other words, $G(p_2) - G(p_1) = \int_{p_1}^{p_2} V(p)dp$

and $G(T_2) - G(T_1) = \int_{T_1}^{T_2} S(T)dT$



Gibbs Free Energy

A puzzle:

at constant T and p,

$$\Delta G = \Delta E + p\Delta V - T\Delta S$$

Assume everything is reversible.

$$\Delta E = w + q$$
$$\Delta S = q/T$$

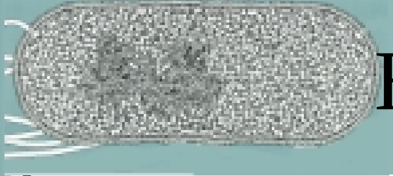
so $\Delta G = w + p\Delta V$

but $w = -p\Delta V$

Hence, $\Delta G = 0$???

According to this, we can’t ever have ΔG < 0 if everything is reversible at constant T and p. But what about all those chemical reactions? Surely they can be run reversibly! But $\Delta G \neq 0$

Where is the mistake?



Homework: For Next WEEK!

This is an early announcement for the homework for Monday. It might be changed slightly. But its good practice for the exam.

1-3) TSW 3.1, 3.3, 3.7

4) Sketch all possible arrangements of

    a) Two balls in six cells

    b) Four balls in six cells

    c) For each of A and B, what is the probability that half the balls will be in the first three cells and half in the second three?

Assume the balls are indistinguishable and the cells may contain only one ball.